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Japanese Published Unexamined (Tokkyo Kokai Koho) Patent Application (A) No. 01-254764, published October 11, 1989; Application No. 63-81856, filed April 1, 1988; Int. Cl.: C 08 79/00, C 08 K 5/42, H 01 B 1/12; Inventor(s): Uushi Ookawa; Assignee: Nitto Electrical Engineering, Inc. (Nitto Denko Kabushikigaisha); Japanese Title: Water-Soluble Conductive Organic Polymers and Manufacturing Method Therefor

**WATER-SOLUBLE CONDUCTIVE ORGANIC POLYMERS
AND MANUFACTURING METHOD THEREFOR**

CLAIM(S)

1) A method to manufacture water-soluble conductive organic polymer having conductivity 10^{-6} S/cm or higher, wherein oxidized polymer of aniline or its derivative contains water-soluble organic macromolecular proton acid.

2) A method to manufacture water-soluble conductive organic polymer having conductivity 10^{-6} S/cm or higher and containing water-soluble organic macromolecular proton acid as a dopant, by polymerizing aniline, its derivative, or its salt by oxidation using an oxidant, characterized in that aniline, its derivative, or its salt is chemically polymerized by oxidation using an oxidant having standard electrode potential 0.6 V or higher, which is defined as an electromotive force for a reducing half-cell battery reaction that uses a standard hydrogen electrode as a reference, and water-soluble organic macromolecular proton acid having acid dissociation constant pK_a 3.0 or lower.

DETAILED DESCRIPTION OF INVENTION

(Field of Industrial Application)

The present invention pertains to a method to manufacture the water-soluble conductive organic polymer, more specifically a method to manufacture the water soluble conductive organic polymer by chemically oxidizing the polymer of aniline or its derivative.

(Prior Art)

Regarding the manufacturing method of conductive organic polymer from aniline or its derivatives, Japanese Unexamined Patent Applications 62-230825 and 62-149724 have disclosed the method to produce a film by electrolytically polymerizing aniline by oxidation on an electrode. By this electrolytic polymerization by oxidation, a polymer film with excellent conductivity can be produced, but this method requires higher cost than chemical polymerization by oxidation, therefore, is not suitable for mass production.

There is another publicly well-known method, wherein conductive organic polymer having conductivity 10^{-6} S/cm and containing an electron receptor as a dopant is manufactured by chemically polymerizing aniline, its derivative, or its salt by oxidation in an oxidized solution containing an oxidant. Also, Japanese Unexamined Published Patent Application 61-258831 discloses that, in manufacturing conductive organic polymer by chemical polymerization by oxidation, the oxidant used preferably has the standard electrode voltage 0.6 V,

which is defined as an electromotive force for a reduction half-cell reaction [??] that uses a standard hydrogen electrode as a reference.

The aforementioned conductive organic polymer produced by chemical polymerization by oxidation, however, is insoluble in water or organic solvent, and is difficult to form it into a film.

Moreover, Japanese Unexamined Published Applications 59-098165 and 62-164730 introduce polyaniline produced by doping polymer anion, but these inventions aim to improve the physical property of polyaniline by adding polymer anion, so their polymerization methods use electrolytic polymerization by oxidation.
(Problems of the Prior Art to Be Addressed)

The inventors, to solve the aforementioned problems in the conductive organic polymer made of oxidized polymer of aniline or its derivative, assiduously studied on how to provide water-solubility to this conductive organic polymer, and found that the water-soluble conductive organic polymer can be produced by chemically polymerizing aniline or its derivative by oxidation in the presence of water-soluble organic macromolecular proton acid and by adding a dopant to this conductive organic polymer.

(Means to Solve the Problem)

The present invention present a method to manufacture the water-soluble conductive organic polymer containing the water-soluble organic macromolecular proton acid as a dopant and having conductivity 10^{-6} s/cm or higher, by chemically

polymerizing aniline, its derivative, or its salt by oxidation by use of an oxidant. The method is characterized in that aniline, its derivative or its salt is chemically polymerized by oxidation by use of an oxidant having the standard electrode potential 0.6 V or higher, which is defined as an electromotive force for a reducing half-cell battery reaction that uses the standard hydrogen electrode as a reference, and water-soluble organic macromolecular proton acid having acid dissociation constant pka 3.0 or less.

The method of the present invention uses an oxidant prepared by combining an oxidant having standard electrode potential 0.6 V or higher defined as an electromotive force for a reducing half-cell battery reaction that uses the standard hydrogen electrode as a reference and water-soluble organic macromolecular proton acid having acid-dissociation constant pka 3.0 or less. By using this combined oxidant, aniline, its derivative or its salt (hereinafter called monomer), is polymerized by oxidation. By so doing, water-soluble conductive organic polymer containing said water-soluble organic macromolecular proton acid as a dopant can be manufactured.

The oxidant used in the aforementioned method needs to have oxidation capability to oxidize a monomer by oxidation, and such an oxidant needs to have the standard electrode potential of 0.6 V or higher that is defined as an electromotive force for a reduction half-cell reaction using a standard hydrogen electrode as a reference, as described in Japanese Unexamined Published Application 61-258831.

If the proton interferes with the reduction half-cell reaction, as in $\text{Cr}_2\text{O}_7^{2-}$, the standard electrode potential in the reaction with which the proton interferes is used as the standard electrode potential in the method of the present invention. This standard electrode potential is described in "CRC Handbook of Chemistry and Physics" (CRC Press, Inc., D-155-D-160) or "Directory of Electrochemistry" by Electrochemical Society (Maruzen, Inc., pp. 71-74).

As the oxidant that meets the aforementioned conditions, any of the following can be used: hydrogen peroxide; permanganate; lead dioxide; bichromate; manganese dioxide; persulfate. They are used in form of solid or liquid.

In the method of the present invention, said oxidant is preferably used by the equivalent amount to the amount of monomer to be polymerized by oxidation. If the amount exceeds said equivalent amount, the excessive oxidant will remain in the reaction system, undercutting the electrical characteristics of the conductive organic polymer.

Also, in the method of the present invention, the water-soluble organic macromolecular proton acid that becomes a dopant when provided with proton, as mentioned earlier, needs to have the acid dissociation constant pK_a 3.0 or less so that it can dope the oxidized polymer produced from the monomer. If macromolecular proton acid having an acid dissociation constant higher than 3.0 pK_a , the produced oxidized polymer cannot be doped, so the conductive organic polymer with conductivity 10^{-6} S/cm or higher cannot be produced. Moreover, with the

macromolecular proton acid used in the present invention, its 0.5 g/dl solution preferably has logarithmic viscosity 0.05 or higher at 30 . If the mol weight of the proton acid is too low, the proton acid will be partially dissociated from the conductive organic polymer when the produced conductive organic polymer is dissolved in water, failing to dissolve the conductive organic polymer.

As to the water-soluble organic macromolecular proton acid with the acid dissociation constant pK_a 3.0 or less used in the method of the present invention, any of following multivalent sulfonic acids of macromolecular polymer can be used: polyvinyl sulfonic acid; polystyrene sulfonic acid; polyvinyl sulfuric acid; polystyrene sulfonic acid; polyvinyl sulfonic acid; polyaryl sulfonic acid; polymethyl methacryl sulfonic acid; poly-2-acrylamide-2-isobutane.

These water-soluble organic macromolecular proton acids may be purchased on the market, or the market-sold monomer may be put to radical polymerization by a conventional method. When the alkali metal salt of the organic macromolecular proton acid is put to a conventional acid treatment or ion-exchange treatment, the organic macromolecular proton acid can be produced as the dissociated acid.

The equivalent amount of water-soluble organic macromolecular proton acid to the amount of the monomer is needed to dissolve the monomer in water, and it is desirably the amount more than that of the oxidant. However, as mentioned earlier, in addition to the macromolecular proton acid used for dissolving the monomer in

water, the proton is discharged from the monomer in the process of polymerization by oxidation, so even if the amount of the oxidant is less than the equivalent amount of the monomer, the polymerization by oxidation can still be performed. Therefore, in the method of the present invention, the amount of the macromolecular proton acid to be used is not specified, but it is preferable to use the amount equivalent to that of the monomer that is needed to dissolve the monomer in water and to use the mol weight 0.3-3 times the macromolecular proton acid [sic].

When the macromolecular proton acid concentration is high in the reaction solution, the solution excessively absorbs the proton at the time of polymerization and is gelatinized, although this varies depending upon the mol weight. As a result, the oxidized polymer that is not soluble in water tends to be produced, so the macromolecular proton acid is preferably used with low concentration in the reaction. If macromolecular proton acid with mol weight nearly 500,000, which is prepared by making sodium polystyrene sulfonate an acidic type by ion-exchange, as the macromolecular, the concentration in the reaction solution is preferably 0.3 mol/l or less.

In the present invention, other than said macromolecular proton acid, low molecular proton acid having the dissociation constant pK_a 3.0 or less can also be used. The low molecular proton acids that can be used are: phenol group such as hydrochloric acid, sulfuric acid, nitric acid, perchloric acid, hydrofluoroboric acid, hydrofluorophosphoric acid, and picric acid; various organic sulfonic acids;

monochloroacetic acid; dichloroacetic acid; nitrobenzoic acid; tartaric acid. The amount of the low molecular proton acid varies depending on the mol weight of the macromolecular proton acid; e.g., a large amount is used when the mol weight of the macromolecular proton acid is high and a small amount when the mol weight of the macromolecular proton acid is low. For example, as mentioned above, if the high macromolecular proton acid with mol weight nearly 50,000, which is prepared by making sodium polystyrene sulfonate acidic type by ion exchange, is used, nearly 70% of the necessary amount may be replaced with low molecular proton acid, but the water-soluble conductive organic polymer can still be produced. However, if the amount exceeding 70% is replaced with low molecular proton acid, cracks may be generated in the film since the conductive organic polymer film is dependent upon the film forming capability of the macromolecular proton acid.

In the method of the present invention, aniline is preferred as the monomer to be used, but alkyl aniline, such as 0-methyl aniline, m-methyl aniline, 0-ethyl aniline, or m-ethyl aniline may also be used. When these monomers are used as a salt, the salt is used as the same salt as that of the same proton acid for doping the oxidized polymer.

In the method of the present invention, as a medium for the reaction, one selected out of water, hydrophilic organic solvent, and hydrophobic organic solvent, can be used or two of them may be combined for use. But, if aniline or water-soluble salt of alkyl aniline is used, water that dissolves water-soluble salt, a

hydrophilic organic solvent or admixture of both is generally used as the medium. When aniline or alkyl aniline per se is used, a hydrophilic organic solvent or hydrophobic organic solvent capable of dissolving it is used as the reaction medium. It is important that said organic solvent should not be oxidized by the oxidant used. As for the hydrophilic organic solvent, a ketone group, such as acetone, tetrahydrofuran, and acetic acid, an ether group, an organic acid group, or an alcohol group can be used. As to the hydrophobic organic solvent, chloroform, carbon tetrachloride, or hydrocarbon can be used.

In a preferred manufacturing method of the conductive organic polymer of the present invention, aniline, alkyl aniline or its salt is dissolved in the reaction medium containing water-soluble organic macromolecular proton acid and polymerized by oxidation by adding an oxidized solution (the solution containing an oxidant, proton acid, and the reaction medium) to said solution. Or the desired amount of oxidant (liquid or powder) may be added to the solution in which aniline, its derivative or its salt and the proton acid are dissolved. Or, the solution in which aniline, its derivative, or its salt is dissolved may be added to the oxidized solution. The proton acid can be added to the solution and/or oxidized solution containing aniline or its derivative.

The reaction temperature is not specifically limited as long as it is lower than the boiling point of the solvent. But, the higher the reaction temperature is, the

lower the conductivity of the oxidized polymer is, so a normal temperature is preferred in order to produce the polymer with high conductivity.

In the method of the present invention, in some cases, the polymer is deposited immediately after the oxidized solution has been added, but, in most cases, the reaction begins after some period of induction, and subsequently the polymer is deposited. In either case, the reaction is completed in a short period of time. Then, it may be agitated for a few minutes - a few hours for maturing. The produced reaction solution is generally used as it is or after having been condensed, for a doping solution, film formation, or for applying over a substrate.

However, when the produced water-soluble conductive organic polymer is separated, the reacted admixture is put into an organic solvent to filter the polymer, and subsequently, the polymer is dissolved in water, again put into the organic solvent for sedimentation, and is collected. By this repetitive sedimentation, the polymer can be refined. Subsequently, by vacuum-drying the polymer, the conductive organic polymer of the present invention can be manufactured.

The conductive organic polymer produced by chemically polymerizing aniline, its derivative, or its salt by oxidation is expressed by the following formula. [The chemical bond structure is attached to the last page of the translation.) It is a linearly structured polymer having repeated units of quinonediimine and contains water-soluble organic macromolecular proton acid as the dopant, so its conductivity is 10^{-6} S/cm or higher.

The oxidized polymer of aniline or its derivative of the present invention has normally a green or dark green color it is liquid or powder. When it is in powder form, the higher its conductivity is, the brighter the green looks, but after molded, it looks radiant blue.

(Advantage of the Invention)

As explained above, by the present invention, the conductive organic polymer produced by the present invention is provided with water-soluble organic macromolecular proton acid as a dopant. This macromolecular proton acid includes multiple water-soluble radicals that do not interfere with the doping, e.g., in case of polystyrene sulfonic acid, the water-solubility seems to be provided by sulfonic acid radical. With the conductive organic polymer of the present invention, the molecular chain of the macromolecular proton acid bonded to the polymer as the dopant is mutually interlaced, so the macromolecular proton acid is not dissociated from the polymer when the conductive organic polymer is dissolved in water and undoped.

Accordingly, the conductive organic polymer of the present invention can be put into film form easily when its solution is applied over a proper substrate by flow-coating.

With the prior art conductive organic polymer made of oxidized polymer of aniline, it is doped or undoped when the polymer confines or discharges the electrolytic ions having negative charge. On the other hand, with the conductive

organic polymer of the present invention, the macromolecular proton acid having negative charge is not dissociated from the polymer at the time of undoping by reduction, so the polymer confines ions having positive charge and neutralizes the macromolecular proton acid.

(Embodiment)

An embodiment of the present invention is explained below, but the present invention is not limited to the scope of the following embodiment.

Embodiment Example 1

A sodium polystyrene sulfonate 20% solution (PS 5 by Toso, Inc., mol weight 50,000-100,000) 50 ml was diluted with 1 l of distilled water, and treated by H-type cationic resin exchange (Dow EX 50W X 12 made by Dow Chemical, Inc.) in a column. Thus, the distillate containing polystyrene sulfonic acid was produced. This distillate 3 l was condensed to nearly 250 ml by a rotary evaporator.

By using phenolphthalein as an indicator, said condensed solution 1.50 ml [sic] used 0.01 N sodium hydroxide solution 36.4 ml for its neutralizing titration, so the concentration of the polystyrene sulfonic acid was 0.243 mol/l.

Ammonium dichromate 0.366 g (0.0013 mol) was dissolved in 20 ml of distilled water. Separately from this, 50 g of distilled water and said polystyrene sulfonic acid solution 93.3 ml (0.023 mol) were put into a 300 ml capacity glass beaker, and to this solution, aniline 0.373 g (0.004 mol) was added and dissolved by agitation. This admixture was cooled by ice to 5 C, and to this cooled admixture,

said ammonium dichromate solution was gradually added little by little. In a few minutes, the reaction solution indicated a green color. When adding of the ammonium dichromate was completed in 30 minutes, said reaction admixture was agitated for 1 hour. The dark green solution thus produced was condensed by a rotary evaporator, and this condensed solution was applied over a polyethylene terephthalate film by a flow-coating method to produce said aniline oxidized polymer. This film was moisture-absorbent; it was recognized that it absorbed moisture when left in the air after having been dried. When this moisture-absorbent film 0.374 g was left in a vacuum desicator until it reached its constant weight, its weight was 0.300 g, and the absorbed moisture in the film was 25%.

The dried film had a 20 μ m thickness and easily dissolved in water. The dried film was easily broken by an external force, but the film absorbed the moisture was pliable and sufficiently durable when handled in various ways.

A copper foil strip with a 1 mm width was bonded with a graphite paste to each of the 4 corners of said dried film with a 1 cm² size, respectively. Its conductivity measured in the air by a Van der Pol method was 2.1×10^{-2} [The superscript assumed for illegibility.] S/cm.

Embodiment Example 2

Into the glass beaker of 300 ml capacity, 50 g of distilled water, a 0.104 mol/l polystyrene sulfonate solution (PS 50 by Toso, Inc., mol weight 400,000 - 600,000) 67.0 ml (0.0069 mol) and hydrofluoroboric acid (0.017 mol) 3.57 g were supplied,

and aniline 0.373 g (0.004 mol) was added to this admixture. A solution prepared by dissolving ammonium dichromate 0.336 g (0.0013 mol) in distilled water 20 ml was gradually added little by little to the solution containing polystyrene sulfonic acid and agitated.

In a few minutes, the reaction solution indicated a green color. In 30 more minutes, adding of the ammonium dichromate solution was completed, and the reaction admixture was agitated for 1 hour. Subsequently, the reaction admixture was filtered to remove the solid composition. The produced dark green reaction solution was condensed by a rotary evaporator and was applied over a polyethylene terephthalate film by flow coating to produce the oxidized polymer film of aniline. This film had a 40 μ m thickness and its conductivity was 7.4×10^{-2} cm.

Embodiment Example 3

Into a 300 ml capacity glass beaker, 100 g of distilled water, 0.777 mol/l polystyrene sulfonic acid solution 16.2 ml (0.013 mol) (PS 50 made by Toso, Inc., mol weight 400,000 - 600,000) and aniline 0.373 g (0.004 mol) were supplied.

This solution was cooled by ice to 5 C and, to this solution containing said polystyrene sulfonate, a solution prepared by dissolving ammonium dichromate 0.336 g (0.0013 mol) in 20 ml of distilled water was gradually added little by little.

In a few minutes after adding of said ammonium sodium dichromate had began, the reaction solution indicated a green color. In 30 more minutes, adding of the ammonium sodium dichromate solution was completed, and this solution was

agitated for 1 hour. After the reaction, the produced dark green reaction solution was condensed by a rotary evaporator and was applied over a polyethylene terephthalate film. Thus, the oxidized polymer film of aniline was manufactured.

This film was 25 μ m thick, and its conductivity was 1.3×10^{-3} S/cm.

In the bond structure, R indicates hydrogen group or alkyl group.